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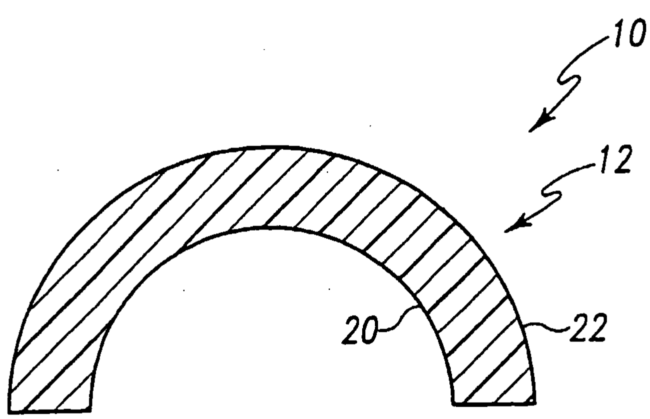
(54) Title: SUPERCRITICAL FLUID TREATMENT OF IRRADIATED POLYETHYLENE



(57) Abstract: A process for forming an orthopaedic implant prosthesis bearing (10) includes the step of quenching a residual free radical population present in an irradiated polyethylene preform or bearing (10) with a supercritical fluid.

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SUPERCRITICAL FLUID TREATMENT OF IRRADIATED POLYETHYLENE

FIELD OF THE INVENTION

The present invention relates to a process for forming orthopaedic implant prosthesis bearings of cross-linked polyethylene, high density polyethylene, high molecular weight polyethylene, high density high molecular weight polyethylene, and ultrahigh molecular weight polyethylene having increased wear resistance and improved mechanical properties. The present invention particularly relates to processes using supercritical fluid-treatment of irradiated polyethylenes.

BACKGROUND OF THE INVENTION

Ultrahigh molecular weight polyethylene (UHMWPE) has been the material of choice for articulating surface applications for three decades. Such UHMWPE resin is commonly used for implantable prosthesis bearings, such as acetabular bearings, glenoid bearings, tibial bearings, and the like, for use in hip, shoulder, knee, and elbow prostheses. The bearings may be formed from polyethylene by direct compression molding processes or by machining the required bearing shapes from mill shapes such as sheet or bar stock. Molding processes may be performed on unirradiated or irradiated polyethylene. Over time, many improvements have been introduced in regard to the fabrication of such bearings, most notably irradiation of the polyethylene to induce cross-linking. In fact, the improved wear characteristics of the polyethylene have been largely attributed to such cross-linking procedures. Typically, a bar stock or preform, or a molded or machined bearing, is irradiated and subsequently heat treated or heat annealed. The irradiation generates molecular cross-links and free radicals. Such cross-linking creates a 3-dimensional network in the polymer which renders it more resistant to abrasive wear in multiple directions. In addition, the free radicals formed upon irradiation of UHMWPE can also participate in oxidation reactions, which reduce the molecular weight of the polymer via chain scission, leading to degradation of physical properties, embrittlement, and an increase in wear rate. The free radicals may be very long-lived, often several years, so that oxidation can continue over an extended period of time. Processes that tend to substantially eliminate residual free radicals induced

by such irradiation tend to provide polyethylene with improved oxidation resistance. Typical processes for quenching free radicals in polyethylene induced by irradiation involve elimination of the free radicals with heat treatments, as well as prolonged exposure of the irradiated polyethylene to stabilizing gases such as hydrogen. Such process steps may serve to accelerate free radical recombination as well as additional crosslinking reactions in the polymer.

Reference is made to a number of prior art references as follows:

1. U.S. Patent No. 5,728,748, and its counterparts all relating to the same application, "Non-Oxidizing Polymeric Medical Implant," to Sun, et al.

2. U.S. Patent No. 5,879,400, "Melt-Irradiated Ultra High Molecular Weight Polyethylene Prosthetic Devices," to Merrill et al.

3. U.S. Patent No. 6,017,975, "Process for Medical Implant of Cross-Linked Ultrahigh Molecular Weight Polyethylene Having Improved Balance of Wear Properties and Oxidation Resistance," to Saum, et al..

4. U.S. Patent No. 6,228,900, "Crosslinking of Polyethylene for Low Wear Using Radiation and Thermal Treatments," to Shen et al.

5. U.S. Patent No. 6,168,626, "Ultra High Molecular Weight Polyethylene Molded Article for Artificial Joints and Method of Preparing the Same," to Hyon et al.

6. U.S. Patent No. 6,245,276, "Method for Molding a Cross-Linked Preform," to McNulty et al.

7. U.S. Patent No. 6,281,264, "Chemically Crosslinked Ultrahigh Molecular Weight Polyethylene for Artificial Human Joints," to Salovey et al.

8. U.S. Patent No. 5,753,182, "Method for Reducing the Number of Free Radicals Present in Ultrahigh Molecular Weight Polyethylene Orthopedic Components ," to Higgins.

The above references teach the general concepts involved in forming or consolidating polyethylene resin directly into a component or a stock form from which the component is made, gamma or other irradiation of the component or the stock form, subsequent heat treating (including annealing or remelting) of the component or stock form, and conventional methods of quenching of the component or stock form. The above references also teach the general concepts of compression

molding and the appropriate apparatuses used therein. The disclosures of these above-listed references are incorporated herein for purposes of establishing the nature of polyethylene resin, the irradiation processes and options, and heat treating processes and options.

SUMMARY OF THE INVENTION

The present invention provides polyethylene bearings with improved mechanical properties, improved oxidation resistance, and increased wear resistance. The polyethylenes prepared by the processes of the present invention can also reduce the amount of wear debris generated from such bearings. Typically, the polyethylene may be ultrahigh molecular weight polyethylene (UHMWPE), although it will be appreciated that the processes of the present invention may be used with various types of polyethylene. The term "polyethylene," as defined herein, includes polyethylene, high density polyethylene, high molecular weight polyethylene, high density high molecular weight polyethylene, ultrahigh molecular weight polyethylene, or any other type of polyethylene utilized in the construction of a prosthetic implant.

The present invention is directed to a process for preparing polyethylene suitable for applications requiring high resistance to abrasive wear. In particular, the present invention is directed to a process for preparing polyethylene suitable for articular surfaces and orthopaedic bearings by treating an irradiated polyethylene with a supercritical fluid (SCF). What is meant herein by the term "bearing" is an orthopaedic implant prosthetic bearing of any type, condition, shape, or configuration. The SCF treatment is performed at appropriate temperatures and pressures consistent with forming supercritical fluids, as described below. Optionally, the SCF may be mixed with other permanent gases, such as hydrogen, nitrogen, and the like during the free radical quenching process.

In some embodiments, preforms for the fabrication of prosthesis bearings may be made from consolidated polyethylene stock which has been irradiated. In other embodiments, the polyethylene stock may be pre-annealed or pressure crystallized, or a combination thereof, to further enhance its mechanical properties. In still other embodiments, instead of a preform, a formed bearing is cross-linked by irradiation and SCF-quenched as described below.

The present invention further pertains to improved cross-linked polyethylene that can be made by the processes described herein. In particular, ultrahigh molecular weight polyethylene (UHMWPE) prepared by the processes of the present invention illustratively exhibits high yield strength, high ultimate tensile strength, and high impact resistance. UHMWPE prepared by the processes of the present invention can exhibit a swell ratio of about 5 or less and a percent elongation to break of about 250% or greater, or preferably a percent elongation to break of about 300% or greater. It is appreciated that a percent elongation to break greater than about 400% may be achieved under certain conditions. This UHMWPE also has a low residual free radical population, thus possessing oxidation resistance comparable to UHMWPE prior to irradiation. Bearings fabricated from UHMWPE prepared by the processes described herein can exhibit increased wear resistance and improved mechanical properties.

Additional features of the present invention will become apparent to those skilled in the art upon consideration of the following detailed description of invention exemplifying the best mode of carrying out the invention as presently perceived.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view of an implantable prosthetic bearing that may be produced by processes described herein;

Fig. 2 is a perspective view of an implantable glenoid bearing prosthesis that may be produced by processes described herein;

Fig. 3 is a perspective view of an implantable acetabular bearing prosthesis that may be produced by processes described herein;

Fig. 4 is a perspective view of an implantable tibial bearing prosthesis that may be produced by processes described herein; and

Fig. 5 is a pressure-temperature phase diagram which illustrates the critical point and the associated supercritical fluid region.

DETAILED DESCRIPTION OF THE INVENTION

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof have been shown by way of example in the drawings and will herein be described in detail. It should be understood, however, that there is no intent to limit the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

A typical prosthetic bearing design includes an articulating or bearing surface on which either a natural bone structure or a prosthetic component articulates. In addition, a typical prosthetic bearing design also includes an engaging surface which may include locking features in the form of mechanisms such as pins, tabs, tapered posts, or the like for locking or otherwise securing the bearing to either another component associated with a prosthetic assembly (e.g., a metal shell or tray) or to the bone itself.

Referring now to Figs. 1-4, there is shown an implantable prosthetic bearing 10. The bearing 10 is shown schematically as a bearing 12 in Fig. 1, whereas specific exemplary embodiments of the prosthetic bearing 10, such as a glenoid bearing 14 for implantation into a glenoid of a patient (not shown), an acetabular bearing 16 for implantation into an acetabulum of a patient (not shown), and a tibial bearing 18 for implantation into a tibia of a patient (not shown) are shown in Figs. 2-4, respectively. Each of the embodiments of the prosthetic bearing 10 includes an articulating or bearing surface 20 on which a natural or prosthetic component bears. For example, in the case of the glenoid bearing 14, a natural or prosthetic humeral head (not shown) bears on the articulating surface 20. Similarly, in the case of a acetabular bearing 16, a natural or prosthetic femoral head (not shown) bears on the articulating surface 20. Moreover, in the case of the tibial bearing 18, a pair of natural or prosthetic femoral condyles (not shown) bear on the articulating surface 20.

Each of the prosthetic bearings 10 also includes an engaging surface 22 which may have a number of features defined therein for engaging either another prosthetic component or the bone into which the bearing 10 is to be implanted. For example, in the case of the glenoid bearing 14, a number of pins or pegs 24 may be

defined in the engaging surface 22 thereof. The pegs 24 are received into a number of corresponding holes (not shown) formed in the glenoid surface of the patient. The pins 24 are typically held in place with the use of bone cement. Moreover, if the glenoid bearing 14 is utilized in conjunction with an implanted metal shell, the engaging surface 22 of the bearing 14 may be configured with a tapered post (not shown) or the like for securing the glenoid bearing 14 to the shell.

In the case of the acetabular bearing 16, a number of keying tabs 26 are defined in the engaging surface 22 along the outer annular surface thereof. The keying tabs 26 are received into a number of corresponding keying slots (not shown) defined in an implanted metal acetabular shell (not shown) in order to prevent rotation of the acetabular bearing 16 relative to the implanted shell. In the case of fixation of the acetabular bearing 16 directly to the acetabulum of the patient (i.e., without the use of a metal shell), the engaging surface 22 of the bearing 16 may alternatively be configured with a number of posts or pegs (not shown) which are received into a number of corresponding holes formed in the patient's acetabulum. In such a case, the posts or pegs are typically held in place with the use of bone cement. Moreover, it should be appreciated that the acetabular bearing 16 may be cemented to the patient's acetabulum without the use of posts or pegs on the engaging surface 22 thereof.

In the case of the tibial bearing 18, a tapered post 28 is defined in the engaging surface 22 thereof. The tapered post 28 is received into a corresponding tapered bore (not shown) defined in an implanted tibial tray (not shown) of a knee prosthesis (not shown). It should be appreciated that the engaging surface 22 of the tibial bearing 18 may also be configured with features to allow the tibial bearing 18 to be secured directly to the tibia without the use of an implanted tray (e.g., by use of bone cement). Moreover, it is appreciated that a tibial bearing for use with a tibial tray may also be designed without the use of the post 28.

The present invention pertains to fabrication of such an orthopaedic implant prosthetic bearing 10 from irradiated polyethylene treated with a SCF. Alternatively, a formed bearing may be irradiated and treated with a SCF. In either case, the preform or formed bearing may be fabricated from an olefinic resin, typically a polyethylene resin, such as an ultrahigh molecular weight polyethylene (UHMWPE) resin. It is further appreciated that other polyethylenes such as high

molecular weight polyethylene, high density polyethylene, high molecular weight high density polyethylene, and the like may be fabricated into bearings using the processes described herein. The term "preform" as used herein refers to an article that has been consolidated, such as by ram extrusion or compression molding of polyethylene resin particles into rods, sheets, blocks, slabs, or the like. The term "preform" also includes a preform "puck" which may be prepared by intermediate machining of a commercially available preform. Such preforms may be obtained or machined from commercially available UHMWPE, for example GUR 1050 HP ram extruded UHMWPE rods from PolyHi Solidur (Fort Wayne, Indiana). The starting preform may be pressure recrystallized as described in U.S. Patent 5,478,906 and in U.S. Patent 6,017,975. The starting preform may be optionally annealed, as described in U.S. Patent 6,017,975, prior to irradiation. This pre-annealing step may be conducted in a substantially oxygen-free atmosphere. It is appreciated that the preform of the present invention may be formed from a wide variety of crude or processed plastic resins suitable for use in orthopaedics, that can be converted by manufacture into a finished bearing. It is further appreciated that the current invention contemplates cross-linking of the polyethylene prior to intermediate machining of a commercial stock into a preform puck.

An exemplary embodiment of the present invention includes a process that includes the steps of irradiating a polyethylene preform to form free radicals and cross-link the polyethylene, and treating the irradiated preform with a supercritical fluid (SCF) at temperatures and pressures consistent with such SCF's to substantially eliminate free radicals remaining from the irradiation step. Treatment of the polyethylene with SCF's may effect further cross-linking in the polyethylene. Thereafter a bearing may be formed from the irradiated and SCF-quenched preform. Alternatively, an existing formed polyethylene bearing is irradiated to cross-link the polyethylene and the residual free radicals are subsequently quenched by treatment with a SCF.

Preferred temperatures for processing are such that deformation of the formed bearing does not occur, and preferred pressures are such that they are uniform and thus do not deform the formed bearing. However, in the case of the quenching of a preform or a bearing that requires an additional amount of processing or

manipulation, such as machining, temperatures above the melting temperature of the polyethylene or pressures that are not substantially uniform may be utilized in the processes described herein.

As alluded to above, the preform or formed bearing is generally irradiated, preferably with gamma radiation; however electron beam or x-ray radiation may also be used. The preform or formed bearing is preferably irradiated in the solid state with gamma radiation at a dose from about 0.5 Mrad to about 50 Mrad using methods known in the art. Alternatively, the preform or formed bearing may be irradiated at a dose from about 1.5 Mrad to about 15 Mrad, or from about 5 Mrad to about 10 Mrad. It will be appreciated that doses of radiation lower than about 0.5 Mrad or higher than about 50 Mrad may be used to prepare certain polyethylenes and in variations of the process. The irradiation process is generally performed at room temperature, however higher temperatures may be used. The irradiation process may be optionally performed under vacuum or in an inert or substantially oxygen-free atmosphere by placing the preform in a bag, which includes materials such as aluminum foil, polyethylene, and the like, suitable for such irradiation processes. The bag may be optionally evacuated and the atmosphere substantially replaced with an inert gas such as nitrogen, argon, and the like. It will be appreciated, however, that acceptable results may be achieved for certain bearing configurations when the irradiation process is carried out under atmospheric conditions, i.e., with some oxygen present. Since the processes described herein allow for radiation-cross-linking of the polyethylene preform prior to forming the bearing, low levels of surface oxidation can be tolerated as the oxidized surface can be removed during subsequent machining of the bearing.

It is appreciated that the preform may be "pre-irradiated" prior to use thereof. In particular, it may be desirable for a manufacturer of prosthetic bearings to purchase material (e.g. polyethylene) which has been irradiated or otherwise cross-linked by a commercial supplier or other manufacturer of the material. Such "out-sourcing" of the irradiation process is contemplated for use in the processes described herein.

In any case, after the polyethylene has been irradiated, it is treated with a SCF, at temperatures and pressures consistent with forming supercritical fluids. The

polyethylene is treated with the SCF for a time that is sufficient to recombine substantially all of the free radicals which remain in the material from the irradiation cross-linking process. Such treatment often results in further cross-linking of the polyethylene and its stabilization with regard to oxidation. Supercritical fluids are known to affect the physical dynamics of polymers; in particular, they may effect swelling of polymers. The dissolution and subsequent fractionation of high density polyethylene by supercritical and near-critical propane is disclosed by Watkins *et al.*, in *The Journal of Supercritical Fluids,* 1991, *4*, 24-31, which journal article is hereby incorporated by reference.

A supercritical fluid is defined herein as a substance where, at a particular temperature, defined as the critical temperature (T_c), and at a particular pressure, defined as the critical pressure (p_c), the molar volume of the liquid and gaseous phases of the substance are identical. Thus, the distinction between liquid and gaseous phase has been lost and the resulting substance exists as a homogenous "fluid" phase which possesses properties intermediate between the gaseous and the liquid phases. With reference to Fig. 5, the point on the pressure-temperature phase diagram defined by temperature T_c and pressure p_c is the critical point. Above T_c, the substance can no longer be condensed at any pressure into a liquid phase. The "supercritical region" is defined herein to include pressure and temperature ranges dictated by the area present on the Temperature - Pressure phase diagram bound by extrapolation above and to the right of the critical point, as shown in the solid-outlined box of Figure 5. In addition, the gaseous region below the critical pressure extrapolation along with the liquid region to the left of the critical temperature extrapolation may also, under certain conditions, possess supercritical fluid-like characteristics. As a result, these regions, which are commonly utilized to describe "near-critical fluids" and "subcritical fluids", are therefore contemplated for inclusion into the term "supercritical fluid" as used herein. For example, the region of temperatures and pressures designated in the shaded area of Fig. 5 indicates a region which provides the desirable characteristics of a SCF. Some examples of substances that are useful as supercritical fluids are listed in Table I. The list in Table I is intended to be illustrative only and is not to be interpreted as limiting of the scope or the spirit of substances contemplated to be used in the invention.

Table I. Critical points for selected substances useful as supercritical fluids.

Substance	Critical Temperature (T_c, °C)	Critical Pressure (p_c, psi)
water	374	3210
ammonia	133	1650
Freon 22®	112	598
ethane	32	712
propane	97	624
nitrous oxide	37	1040
carbon dioxide	31	1070
fluoroform	26	711
xenon	17	841

The irradiated polyethylene may also be treated with a SCF mixed with other permanent gases, such as hydrogen, nitrogen, and the like, during the free radical quenching process. The irradiated polyethylene is treated at temperatures and pressures consistent with forming supercritical fluids for such mixtures. The irradiated polyethylene is treated for a time that is sufficient to recombine substantially all of the free radicals which remain in the material from the irradiation cross-linking process, thus further cross-linking the material and stabilizing the polyethylene with regard to oxidation. It is appreciated that the addition of permanent gases or stabilizing gases, such as those described herein, to the SCF may affect the quenching process by having an impact on polymer swelling. In addition, it is appreciated that the addition of permanent gases or stabilizing gases to the SCF may affect the quenching process by effectively lowering the critical temperature or critical pressure relative to the temperature and pressure needed to generate the pure SCF. The component of the stabilizing gas, such as hydrogen gas, may be present in from about 0.1% to about 4% by weight, or from about 0.1% to about 1.9% by weight.

Thermal distortion of the UHMWPE formed bearings during SCF treatment likely does not occur at the modest temperatures required for formation of

many SCF's. Moreover, given the homogeneous nature of SCF's, deformation of the formed bearing is equally unlikely to occur due to the absence of non-uniform forces exerted by the pressures used in the present invention.

The irradiated polyethylene preferably is treated with a SCF selected from a group consisting of hydrocarbons, fluorocarbons, chlorofluorocarbons, carbon dioxide, nitrous oxide, ammonia, water, and xenon. Preferably, the SCF is selected from a group consisting of hydrocarbons, fluorocarbons, and chlorofluorocarbons. More preferably, the SCF is a hydrocarbon. The polyethylene preform or formed bearing is treated at a temperature near the T_c for the given supercritical fluid, preferably at a temperature of about 50°C to about 200°C. The polyethylene preform or formed bearing is treated at a pressure near the p_c for the given supercritical fluid, preferably about 500 psi to about 5000 psi for about 4 hours or less, preferably for about 2 hours or less. It is appreciated that temperatures below 50°C or above 200°C may be desirable for some supercritical fluids in variations of the present process.

An exemplary process includes the irradiation of the preform or formed bearing with a dose of radiation as described above, illustratively from about 1.5 Mrad to about 15 Mrad, followed by treatment with a supercritical hydrocarbon at about 1000 to about 3000 psi, optionally containing hydrogen gas, at about 80°C to about 100°C for a period of about 2 hours or less. The temperature and hold time that is sufficient to eliminate substantially all of the residual free radicals present in the UHMWPE may be determined by measuring the free radical population present in the samples using the electron paramagnetic resonance (EPR). The temperature and hold time are chosen such that the free radical populations measured by EPR, as described below, are decreased by about 90%, preferably decreased by about 95%, or by about 97%, from that population measured by EPR after irradiation and before quenching. Such SCF-quenching treatment after irradiation results in improved molecular mobility, allowing increased cross-linking, and thus, can reduce the oxidation potential of the polyethylene. When conventional heat treatment alone is carried out at comparable temperatures to those used in processes described herein, elimination of free radicals is less complete resulting in higher oxidation potential and increased wear rates.

After SCF treatment, the quenched and cross-linked polyethylene may be cooled, optionally in a substantially oxygen-free atmosphere or vacuum. The cross-linked polyethylene may be cooled to a temperature less than about 50°C, preferably to about room temperature, prior to exposing the polyethylene to air. In the case of a polyethylene preform, after cooling, the preform is formed into a bearing using processes known in the art such as machining or molding. The cross-linked UHMWPE is especially useful as a bearing surface, for example in prosthetic hip joint cups and as other prosthetic shapes for replacement of other joints of the human body, including knees, shoulders, fingers, spine, and elbows. The finished bearing can be packaged and sterilized.

A more complete understanding of the present invention can be obtained by referring to the following illustrative examples or the practice of the invention, which examples are not intended, however, to be unduly limiting of the scope or the spirit of the invention.

EXAMPLES

Example 1. Hydrocarbon SCF swelling of UHMWPE

Test samples consisting of small rods (36 mm long and 4.6 mm in diameter) of ram extruded GUR 1020 UHMWPE from Perplas Medical, Bacup England, were exposed to supercritical propane or supercritical ethane at various temperatures and pressures in a small volume pressure vessel equipped with a view port. The samples were suspended in the pressure vessel (Jerguson Gage, Newport Scientific) near the view port and the dimensional changes (length and diameter) of each sample occurring during contact with the SCF were measured through the view port using calipers.

The data in Table II illustrate the effect of contacting UHMWPE with supercritical ethane or propane at various temperatures and pressures for various lengths of time.

Table II. Percent change in volume of UHMWPE after exposure to supercritical hydrocarbon.

Hydrocarbon	Temperature (°C)	Pressure (psi)	Treatment Time (min.)	Volume Change (%)
ethane	100	1400	30	3
ethane	60-64	2500	45	9
propane	95	2500	45	11
propane	90-92	2400	30	11
propane	100-103	2400	60	16
propane	100-103	2700	30	19
propane	100	2800	10	minimal

Example 2. Hydrocarbon SCF treatment of irradiated UHMWPE.

Test samples consisting of small rods (36 mm long and 4.6 mm in diameter) of ram extruded GUR 1020 UHMWPE from Perplas Medical, Bacup England, were vacuum packaged in heat sealed aluminum foil pouches. The samples were gamma irradiated at a target dose of 5 Mrad at Isomedix, of Whippany, New Jersey. Following irradiation, the samples were removed from the vacuum packages and exposed to supercritical propane or supercritical ethane at various temperatures and pressures in a small volume pressure vessel equipped with a view port. The samples were suspended in the pre-heated pressure vessel (Jerguson Gage, Newport Scientific) and the appropriate gas was introduced until the desired pressure was attained. After treatment with the SCF, each sample was analyzed with a Bruker EMX EPR spectrometer. The samples were inserted into 5 mm quartz EPR tubes for measurement and the assessment of relative free radical concentration was made by integrated intensity.

The data in Table III illustrate the effect of contacting irradiated UHMWPE with supercritical hydrocarbon at various temperatures and pressure for various length of time. A rapid decrease in the EPR signal was observed along with a measured volume increase of 10-12 % while under SCF conditions. After 90 minutes the relative free radical concentration was reduced by at least 90%. In contrast,

irradiated UHMWPE held at 80°C for 90 minutes in an air oven showed only a 69% decrease in the EPR signal.

Table III. Reduction in free radical population present in irradiated UHMWPE after exposure to supercritical hydrocarbon.

Hydrocarbon	Temperature (°C)	Pressure (psi)	Treatment Time (min.)	Reduction in Free Radical Population (%)
ethane	80	1500	135	94
ethane	80	3000	135	95
propane	80	1500	30	90
propane	80	1500	60	90
propane	80	1500	90	92
propane	80	1500	120	91
propane	80	3000	10	94
propane	80	3000	30	90
propane	80	3000	60	90
propane	80	3000	90	90
propane	80	3000	120	91

Example 3. Treatment of irradiated UHMWPE with supercritical hydrocarbon and hydrogen mixture.

The test samples were irradiated as described in Example 2, but following irradiation the test samples were removed from the vacuum packages and exposed to supercritical propane or supercritical ethane containing various weight percentages of hydrogen gas. The samples were suspended in the pre-heated pressure vessel used in Example 2, hydrogen gas was introduced, and the appropriate gas was introduced until the desired pressure was attained. The data in Table IV indicate an improvement in the free radical decay in the presence of hydrogen. It is appreciated

that the slightly higher temperature used may also have contributed to the faster free radical decay rate.

Table IV. Reduction in free radical population present in irradiated UHMWPE after exposure to supercritical hydrocarbon and hydrogen mixtures at 3000 psi.

Hydrocarbon	Hydrogen (Weight %)	Temperature (°C)	Treatment Time (min.)	Reduction in Free Radical Population (%)
– *	100	60	70	78
– **	100	100	40	95
ethane	0.04	80	60	94
ethane	0.21	80	70	93
ethane	1.0	80	90	93
ethane	2.0	80	90	94
ethane	4.1	100	30	97
ethane	4.1	100	60	97
propane	1.9	100	15	97
propane	1.9	100	30	98
propane	1.9	100	60	98
propane	1.9	100	90	98
propane	1.9	100	120	99

* Pure hydrogen gas at 30 psi.

** Pure hydrogen gas at 1850 psi.

Example 4. Comparison of treating irradiated UHMWPE with heat or a supercritical propane and hydrogen mixture.

One set of test samples was again treated as described in Example 3 in supercritical propane containing 1.9 weight % hydrogen at 100°C and 3000 psi. A second set of test samples were irradiated as described in Example 2, but following

irradiation the test samples were treated with heat alone at 100°C in the vacuum package. It is appreciated that hydrogen may be present in such vacuum packages as a consequence of the irradiation step. The data in Table V illustrate a more rapid decay of free radical populations in SCF treated samples compared to conventional heat treatments.

Table V. Reduction in free radical population present in irradiated UHMWPE after exposure to a supercritical hydrocarbon and hydrogen mixture (1.9 weight %) at 100°C and 3000 psi compared to heat treatment alone at 100°C in a vacuum package.

Treatment Time (min)	SC-Propane/Hydrogen (% Reduction)	Oven Heated (% Reduction)
15	97	64
30	98	73
60	98	80
90	98	84
120	99	86

While the invention has been illustrated and described in detail in the drawings and foregoing description, such an illustration and description is to be considered as exemplary and not restrictive in character, it being understood that only the illustrative embodiments have been shown and described and that all changes and modifications that come within the spirit of the invention are desired to be protected.

There are a plurality of advantages of the present invention arising from the various features of the prosthetic bearing and associated processes described herein. It will be noted that alternative embodiments of each of the prosthetic bearings and associated processes of the present invention may not include all of the features described yet still benefit from at least some of the advantages of such features. Those of ordinary skill in the art may readily devise their own implementations of a prosthetic bearing and associated processes that incorporate one or more of the features of the present invention and fall within the spirit and scope of the present invention as defined by the appended claims.

For example, although it has been described herein to cross-link materials via irradiation, a process which has numerous advantages in regard to the present invention, it should be appreciated that certain of such advantages may be achieved by cross-linking the materials by any other suitable technique.

Furthermore, while the processes described herein are presented in the context of quenching free radicals generated during a cross-linking process, such as irradiation, it should be appreciated that such a free radical quenching process may be generally applicable to reducing free radical populations which are present whether or not the polyethylene has been irradiated or otherwise cross-linked.

CLAIMS:

1. A process for preparing an orthopaedic bearing, comprising the steps of:

irradiating a polyethylene preform; and

quenching a free radical population present in the polyethylene preform with a supercritical fluid subsequent to the irradiating step.

2. The process of claim 1, wherein the polyethylene preform includes an ultrahigh molecular weight polyethylene preform.

3. The process of claim 1, wherein the irradiation step is conducted in a substantially oxygen-free atmosphere.

4. The process of claim 1, wherein the irradiation step includes irradiating the preform with a dose of gamma radiation within the range from about 0.5 Mrad to about 50 Mrad.

5. The process of claim 1, wherein the quenching step includes quenching the preform with a supercritical fluid selected from the group consisting of hydrocarbons, fluorocarbons, chlorofluorocarbons, carbon dioxide, nitrous oxide, ammonia, water, and xenon.

6. The process of claim 1, wherein the quenching step includes quenching the preform with a supercritical fluid selected from the group consisting of hydrocarbons, fluorocarbons, and chlorofluorocarbons.

7. The process of claim 1, wherein the quenching step includes quenching the preform with a supercritical fluid selected from the group consisting of ethane and propane.

8. The process of claim 1, further comprising the step of heating the preform prior to the irradiation step.

9. The process of claim 8, wherein the heating step is performed at a temperature greater than the melting temperature of the polyethylene preform and less than the decomposition temperature of the polyethylene preform.

10. The process of claim 8, wherein the heating step includes heating the preform at a temperature within the range from about 250°C to about 360°C for a time of about 0.5 hours or greater.

11. The process of claim 8, wherein the heating step includes heating the preform for a time within the range from about 0.5 hours to about 10 hours.

12. The process of claim 8, wherein the heating step is performed in a substantially oxygen-free atmosphere.

13. The process of claim 8, further comprising the step of cooling the polyethylene preform to a temperature below the melting temperature of the polyethylene preform, where the cooling step is performed after the heating step, and includes cooling the polyethylene preform at a cooling rate of about 40°C per hour or less

14. A process for preparing an orthopaedic bearing, comprising the steps of:

irradiating an ultrahigh molecular weight polyethylene preform with a dose of gamma radiation within the range from about 0.5 Mrad to about 50 Mrad; and

quenching a free radical population present in the preform with a supercritical fluid, the supercritical fluid selected from the group consisting of hydrocarbons, fluorocarbons, and chlorofluorocarbons.

15. The process of claim 14, wherein the irradiation step includes irradiating the preform with a dose of gamma radiation within the range from about 1.5 Mrad to about 15 Mrad.

16. The process of claim 14, wherein the quenching step includes quenching the preform with a hydrocarbon supercritical fluid.

17. The process of claim 14, wherein the quenching step is performed at a temperature within the range from about 50°C to about 250°C for a time of about 4 hours or less.

18. The process of claim 14, wherein the quenching step is performed at a temperature within the range from about 80°C to about 130°C.

19. The process of claim 14, wherein the quenching step is performed at a pressure within the range from about 500 psi to about 4000 psi.

20. The process of claim 14, wherein the quenching step is performed at a pressure within the range from about 1000 to about 3000 psi.

21. The process of claim 14, wherein the quenching step includes quenching the preform with the supercritical fluid and a stabilizing gas.

22. The process of claim 14, wherein the quenching step includes quenching the preform with the supercritical fluid and hydrogen gas.

23. The process of claim 14, wherein the quenching step includes quenching the preform with the supercritical fluid and hydrogen gas within the range from about 0.1% to about 4% by weight.

24. The process of claim 14, wherein the quenching step is effective to reduce the free radical population present in the preform by about 90 percent or greater.

25. The process of claim 14, wherein the quenching step is effective to reduce the free radical population present in the preform by about 95 percent or greater.

26. A process for preparing an orthopaedic bearing, comprising the steps of:

quenching a free radical population present in a cross-linked preform with a supercritical fluid;

cooling the cross-linked preform; and

forming a bearing from the cross-linked preform.

27. The process of claim 26, wherein the quenching step is performed at a temperature within the range from about 80°C to about 130°C for a time of about 2 hours or less.

28. The process of claim 26, wherein the quenching step includes quenching the preform with a supercritical hydrocarbon and hydrogen gas within the range from about 0.1% to about 4% by weight.

29. A process for preparing an orthopaedic bearing, comprising the steps of:

forming the bearing; and

quenching a free radical population present in the bearing with a supercritical fluid.

30. The process of claim 29, wherein the quenching step includes quenching the bearing with a supercritical hydrocarbon.

31. The process of claim 29, wherein the quenching step includes quenching the bearing with the supercritical fluid at a pressure within the range from about 1000 psi to about 3000 psi.

32. The process of claim 29, wherein the quenching step is performed at a temperature within the range from about 80°C to about 130°C for a time of about 4 hours or less.

33. The process of claim 29, wherein the quenching step includes quenching the bearing with the supercritical fluid and a stabilizing gas.

34. The process of claim 29, wherein the quenching step includes quenching the bearing with the supercritical fluid and hydrogen gas within the range from about 0.1% to about 4% by weight.

35. The process of claim 29, wherein the quenching step is effective to reduce the free radical population present in the bearing by about 90 percent or greater.

36. The process of claim 29, wherein the quenching step is effective to reduce the free radical population present in the bearing by about 97 percent or greater.

37. A process for preparing an orthopaedic bearing, comprising the step of:

quenching a free radical population present in a polyethylene preform with a supercritical fluid.

38. The process of claim 37, wherein the quenching step includes quenching an irradiated polyethylene preform.

39. The process of claim 37, wherein the quenching step includes quenching an irradiated polyethylene preform, the preform having been irradiated with a dose of gamma radiation within the range from about 0.5 Mrad to about 50 Mrad.

40. The process of claim 37, wherein the quenching step includes quenching a polyethylene preform with a supercritical fluid selected from the group consisting of hydrocarbons, fluorocarbons, and chlorofluorocarbons.

41. The process of claim 37, wherein the quenching step includes quenching a polyethylene preform with a supercritical fluid and hydrogen gas.

42. A process for preparing an orthopaedic bearing, comprising the step of:

quenching a free radical population present in a cross-linked polyethylene preform with a supercritical fluid.

43. A process for preparing an orthopaedic bearing, comprising the step of:

quenching a free radical population present in an irradiated polyethylene bearing with a supercritical fluid.

44. The process of claim 1, wherein the irradiation step includes irradiating the preform with a dose of gamma radiation within the range from about 0.5 Mrad to about 100 Mrad.

45. A process for preparing polyethylene, comprising the step of:

quenching a free radical population present in the polyethylene with a supercritical fluid.

46. A polyethylene prepared by the process comprising the step of:

quenching a free radical population present in the polyethylene with a supercritical fluid.

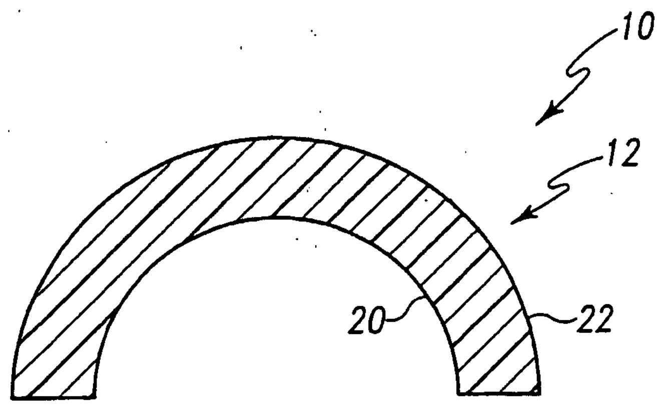

Fig. 1

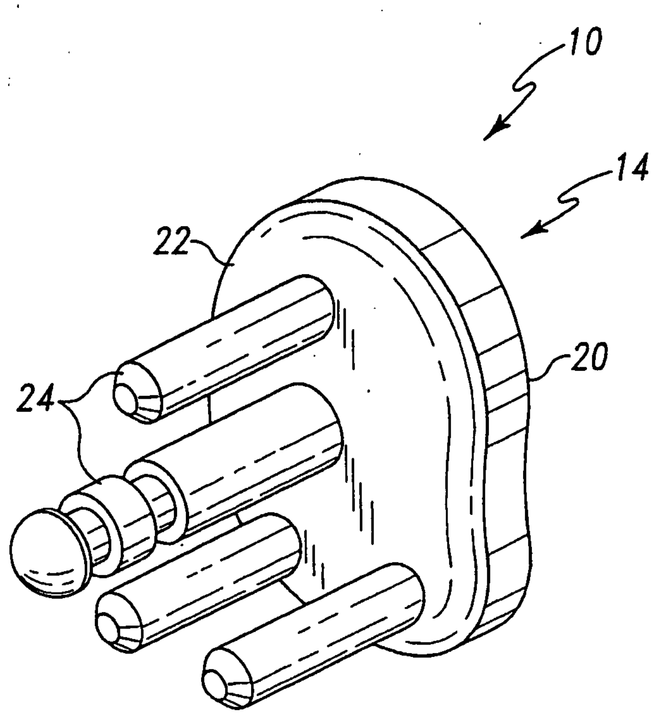

Fig. 2

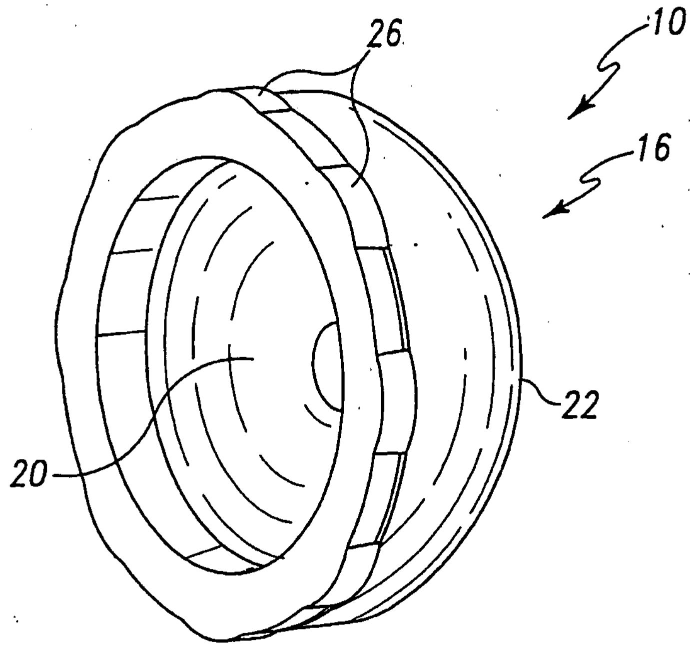

Fig. 3

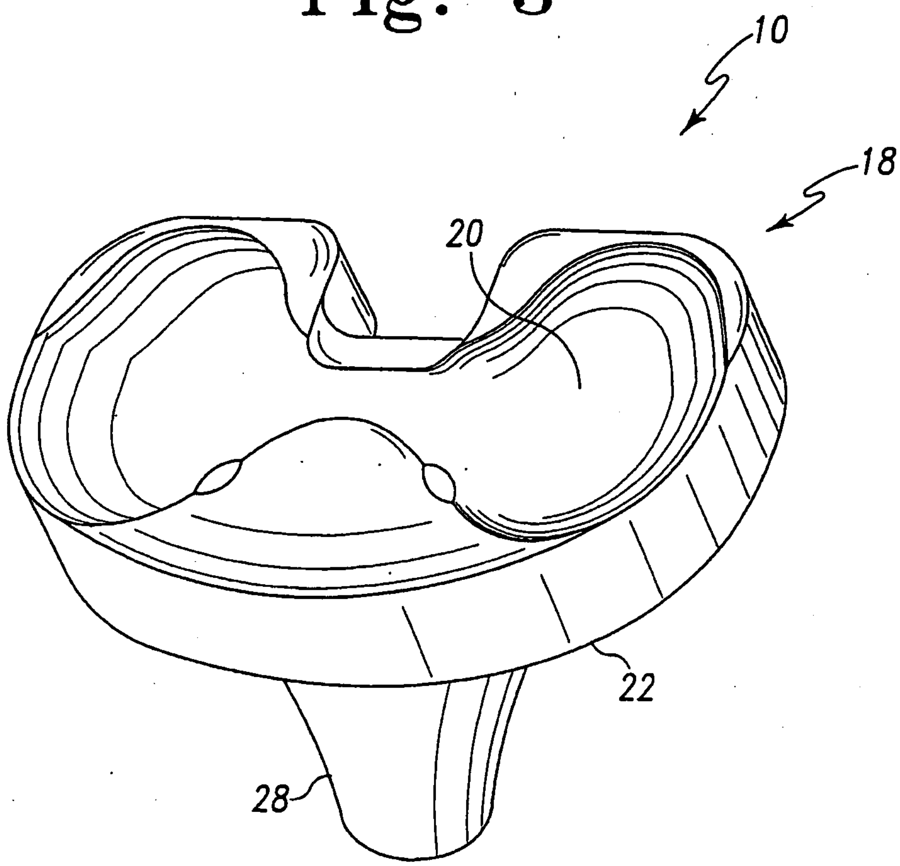

Fig. 4

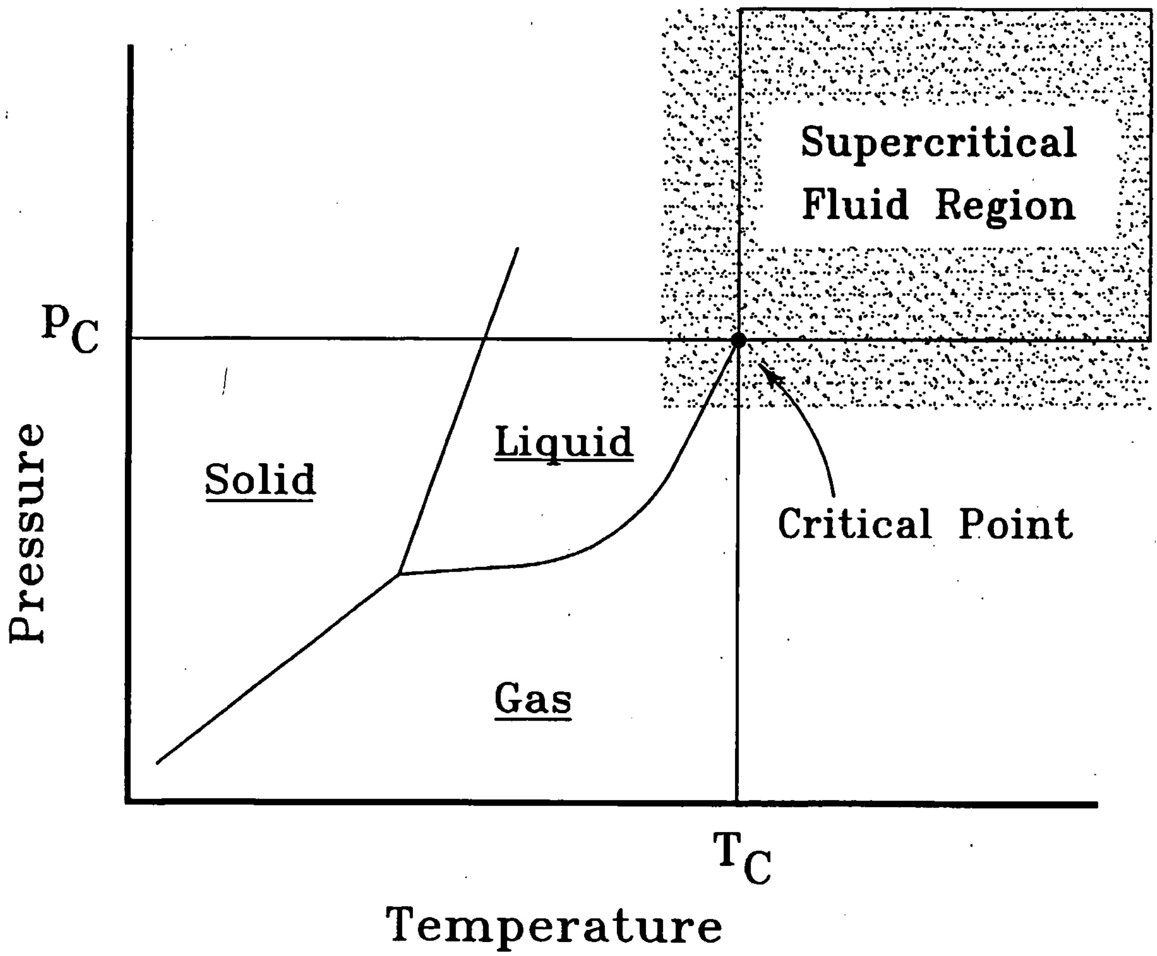
Supercritical
Fluid Region
P_C
Liquid
Solid
Critical Point
Pressure
Gas
T_C
Temperature

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/30582

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B29C 35/08, 43/02, 43/52, 71/00
US CL : 264/488, 85, 232, 237, 322; 526/352

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 264/488, 85, 232, 237, 322

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,607,518 A (HOFFMAN et al) 04 March 1997 (04.03.1997), column 3, lines 46-55; column 4, lines 40-54; column 5, lines 31-42.	45, 46

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search	Date of mailing of the international search report
18 December 2001 (18.12.2001)	11 JAN 2002

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